UNIVERSITI PUTRA MALAYSIA

OPTICAL AND ELECTRICAL PROPERTIES OF TRANSITION METAL CALCIUM PHOSPHATE GLASSES

EMMA ZIEZIE BT. MOHD. TARMIZI.

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By

EMMA ZIEZIE BT MOHD TARMIZI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of Requirement for the Degree of Master of Science

March 2006

For my beloved parents, siblings and family

Mohd Tarmizi Bin Ngah & Hasnah Bt Talib

Azrul Hafizie

Elyana Ziezie

Ahmad Khalis Hafizie

Hamidah Bt Talib & Hatijah Bt Taib

For showering me with love, understanding and encouragement

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree Master of Science.

OPTICAL AND ELECTRICAL PROPERTIES OF TRANSITION METAL CALCIUM PHOSPHATE GLASSES

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March 2006

Chairman : Associate Professor Zainal Abidin Talib, PhD

Faculty : Science

Investigation was carried out between binary and ternary series in order to determine the role of transition metal (TM) ions in calcium phosphate glass. Various transition metal ions in calcium phosphate glass $(TMO)_x$- $(CaO)_{0.30-x}$ $(P_2O_5)_{0.7}$, (TM = Cu, Mn and Zn) in the composition range $0.01 \leq x \leq 0.09$ were prepared by traditional melt quenching technique. Optical absorption, dielectric spectroscopy, X-ray diffraction and Fourier Transform Infrared (FTIR) spectroscopy have been used to characterize the structural, optical and electrical features of the glasses. All of the samples under study have been confirmed to be amorphous by X-ray diffraction (XRD) measurements. Results from FTIR spectroscopy showed that the spectra were dominated by the spectral characteristic of P_2O_5 in a fingerprint region below 1500 cm^{-1}. From the absorption edge studies, the values of optical band gap (E_{opt}) and energy gap (E_g) have been evaluated using Urbach absorbance rule. The values of optical band gap (E_{opt}) recorded for binary CaO-P_2O_5 glasses ranges from 3.578 to 2.114 eV while for ternary series CaO-P_2O_5 doped with Cu_2O, CuO, MnO and ZnO ranging from 2.114 to 1.697 eV, 3.310 to 1.718 eV, 3.030 to 3.279 and from 2.747 to 2.989 eV. Binary and ternary series doped with Cu^+ and Mn^{2+} showed the energy

gap, E_g increased with metal oxide and dopant materials ranges from 0.500 to 1.564 eV, 0.681 to 0.736 eV and from 0.246 to 0.283 eV. $CaO\text{-}P_2O_5$ glasses doped with, Cu^{2+} and Zn^{2+} recorded inverse pattern where the values ranging from 1.863 to 0.600 eV and from 1.172 to 0.744 eV. Optical band gap (E_{opt}) and energy gap (E_g) is suggested to be associated with structural disorder in the sample. A number of physical studies have also been conducted which include refractive index and density. The density of the glass was determined by Archimedes Principle. Refractive Index was determined at 589.3 nm and 632.6 nm and was found to agree with Lorentz-Lorenz equation where the refractive index increased with increase of density of the samples. Dielectric permittivity was measured in the temperature range of 25 to 300°C. Dielectric permittivity and dielectric loss factor for all samples decreased with frequency and increased with temperature between range 1×10^3 to 1 Hz and from 1×10^{-5} to 1×10^{-3} Hz. From the empirical data, other values such as molar volume and molar refractivity have been computed. Ionic refractivity, ionic radii and field strength have been interpreted from the obtained data. It is obvious that the refractive index varies with molar refractivity, which depends on the polarizability of the ions in the samples, density and molecular weight. Those properties were found to be sensitively depends on its compositions.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KAJIAN OPTIK DAN ELEKTRIK BAGI LOGAM PERALIHAN KACA KALSIUM FOSFAT

Oleh

EMMA ZIEZIE BT MOHD TARMIZI

Mac 2006

Pengerusi : Profesor Madya Zainal Abidin Talib, PhD

Fakulti : Sains

Kajian telah dibuat diantara sistem perduaan dan pertigaan dalam menentukan peranan logam peralihan dalam sistem asas kaca fosfat. Pelbagai logam peralihan di dalam kaca kalsium fosfat $(TMO)_x + (CaO)_{0.30-x}(P_2O_5)_{0.7}$, (TM = Cu, Mn and Zn) di dalam komposisi $0.01 \leq x \geq 0.09$, telah dihasilkan menggunakan teknik sepuh lebur. Penyerapan optik, spektroskopi dielektrik, pembelauan sinar-X dan sepktroskopi Jelmaan Fourier Inframerah (FTIR) telah digunakan untuk menggambarkan cirri struktur, optic dan dielektrik yang berlaku dalam semua sampel. Semua sampel dalam pengajian ini telah disahkan sebagai amorfus melalui pengukuran pembelauan sinar-X (XRD). Keputusan spectra FTIR telah didominasi oleh spektra bahan P_2O_5 dalam rantau pencirian 1500 cm^{-1}. Melalui kajian pinggir penyerapan, nilai bagi jurang jalur optik (E_{opt}) dan jurang tenaga (E_g) telah dinilai menggunakan peraturan penyerapan Urbach. Nilai jurang jalur optik (E_{opt}) untuk siri perduaan kaca $CaO-P_2O_5$ dicatatkan bermula dari 3.578 ke 2.114 eV manakala bagi siri pertigaan $CaO-P_2O_5$ yang didop dengan Cu_2O, CuO, MnO dan ZnO bermula dari 2.114 ke 1.697 eV, 3.310 ke 1.718 eV, 3.030 ke 3.279 dan dari 2.747 ke 2.989 eV. Siri perduaan dan pertigaan yang didop dengan Cu^{2+} dan Mn^{2+} menunjukkan jurang

tenaga, E_g bertambah dengan logam oksida dan bahan dop dalam lingkungan nilai 0.500 ke 1.564 eV, 0.681 ke 0.736 eV dan dari 0.246 ke 0.283 eV. Kaca P_2O_5 yang didop dengan Cu^{2+} dan Zn^{2+} mencatatkan sebaliknya dimana bacaan bermula dari 1.863 ke 0.600 eV dan dari 1.172 ke 0.744 eV. Nilai jurang jalur optik (E_{opt}) dan jurang tenaga (E_g) dicadangkan berkaitan dengan struktur rawak dalam sampel. Beberapa pengajian fizikal juga telah dijalankan termasuk indeks biasan dan ketumpatan. Ketumpatan kaca telah diukur menggunakan prinsip Archimedes. Indeks biasan telah diukur pada 589.3 nm dan 632.8 nm dan telah dikenalpasti menepati persaman Lorentz-Lorenz yang mana nilai tersebut meningkat dengan ketumpatan bagi sampel. Ketelusan dielektrik telah diukur pada julat suhu dari 25 hingga 300°C. Data menunjukkan ketelusan dielektrik dan faktor kehilangan dielektrik bagi semua sampel menurun dengan peningkatan frekuensi dan meningkat dengan peningkatan suhu dari linkungan nilai 1 x 10^3 to 1 Hz dan dari 1 x 10^{-5} ke 1 x 10^{-3} Hz. Dari nilai data empirikal yang diukur, nilai-nilai lain seperti isipadu molar dan pembiasan molar telah dikira. Pembiasan ion, jejari ion dan kekuatan medan bahan telah dianggar melalui data yang diperolehi. Jelas sekali bahawa indeks biasan berkadar songsang dengan pembiasan molar yang bergantung kepada pengutuban ion dalam sampel, ketumpatan dan berat molekul. Semua sifat didapati begitu sensitif pergantungannya kepada komposisi bahan tersebut.

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I certify that an Examination Committee has met on 29th March 2006 to conduct the final examination of Emma Ziezie Bt Mohd Tarmizi on her Master of Science thesis entitled "Optical and Electrical Properties of Transition Metal Calcium Phosphate Glasses" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment of the requirement for the Degree of Master of Science. The members of the Supervisory Committee are as follows:

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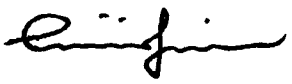

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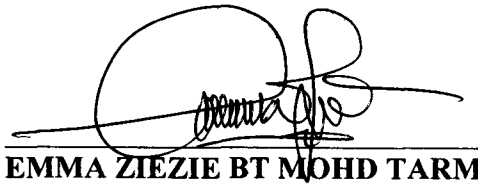
DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



EMMA ZIEZIE BT MOHD TARMIZI

Date : 12 . 06 . 2006

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A	absorption
Ag	silver
α	absorption coefficient
α_e	electronic polarizability
α_I	ionic polarization
α_m	molar polarizability
ϕ	angle
BO	bridging oxygen
β	propagation constant
C	capacitance
c	velocity of light in vacuo ($c = 3 \times 10^8$ ms^{-1})
d	dipole moment
d	thickness
dc	direct current
DBO	double bond
e	electronic charge
ε^*	relative complex permittivity
ε_o	permittivity of free space ($\varepsilon_o = 8.85 \times 10^{-12}$ F/m)
$\varepsilon(0)$	permittivity at low frequency
$\varepsilon(\infty)$	permittivity at high frequency
ε'	permittivity or dielectric constant
ε''	dielectric loss factor

E_g	energy gap
E_{opt}	optical band gap
FTIR	Fourier transforms infrared
G	conductance
$\hbar$	Planck constant ($\hbar$ = 6.6256 x 10^{-34} Js)
I	current
I	light intensity
I_o	initial intensity
K	dielectric constant
LEDs	light emitting diods
LDs	laser diodes
M	mass of particle
Me	metal
M_{TO}	ratio metal per terminal oxygen
MeO	metal oxide
NBO	non-bridging oxygen
NMR	nuclear magnetic resonance
n	refractive index
N_A	Avogadro's number (N_A = 6.023 x 10^{23} mol^{-1})
ρ	density
Q^n	number of the BO atoms in a PO_4 group
Q	charge
R	resistor
R	reflectance
R_m	molar refractivity

R_i	ionic refractivity
T	transmittance
T_g	transformation temperature (^oC)
tan δ	loss angle (measure of dielectric losses)
τ	relaxation time (s)
TM	transition metal
TO	terminal oxygen
V	volume
V	voltage
Y	admittance
y	molar ratio $(Me_{2/v}O)/P_2O_5)$
v	valency of *Me*
V_m	molar volume
λ	wavelength
ω	angular frequency
XRD	x-ray diffraction
Z	impedance

CHAPTER 1

INTRODUCTION

1.1 Introduction

A glass can be defined as an amorphous solid completely lacking in long range order, exhibiting a region of glass transformation behavior and periodic atomic structure. Its atoms are arranged randomly. Therefore it has no unit cell and at most it has only short-range order or locally crystalline.

Glasses generally show optical isotropy, reversible softening and solidification and a certain dependence of their properties on thermal history. Unlike other amorphous substances, they have the general feature (both inorganic and organic glasses) of changing their physical properties (e.g thermal expansion, resistivity) in the transformation region in which the metastable glass melt form glass.

As may be expected, much of the glass science is developed on the basis of the major commercial uses of glass. More than 99% of the commercial tonnage consists of glass compositions that are oxides. A large percentage of these are silica-based. This includes even the highly specialized application of glass to microelectronic packaging where the annual volume of sale may be low but glass is the "value-adding" component, i.e., the application of glass enhances the value of assembly after the incorporating process. It is not surprising when the term "glass" is used in scientific conversation, oxide glasses are usually implied. The chemistry of glass is considered here as a classified survey of findings on